

# 1. Introduction and Aim

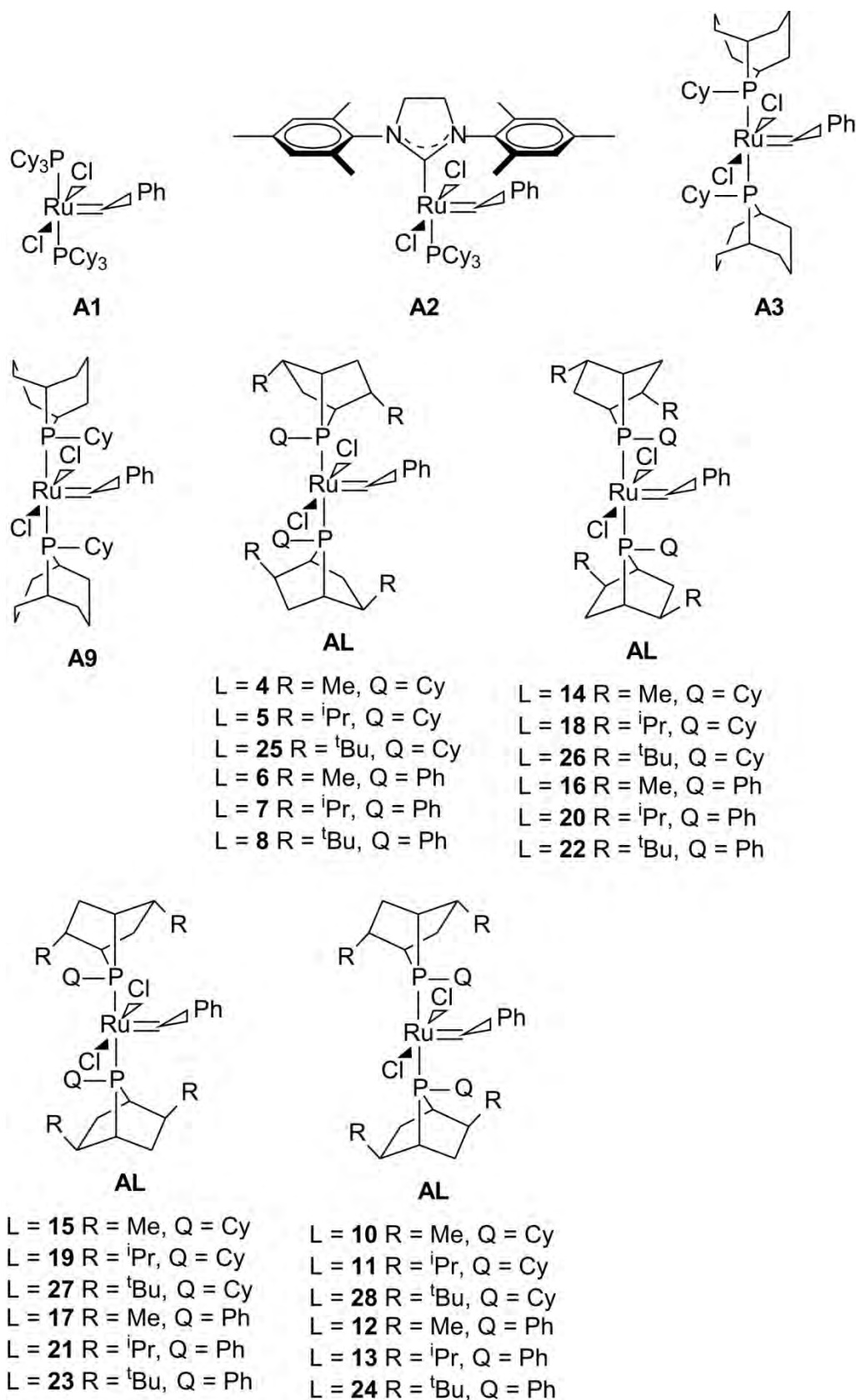
## 1.1 Introduction

Phosphine compounds are used with great success as ligands in the synthesis of a large variety of homogeneous catalyst systems.<sup>1</sup> Hydroformylation,<sup>2-4</sup> hydrogenation<sup>5</sup> and hydrocyanation<sup>6</sup> are but a few examples where phosphine metal complexes are used as catalysts. The ability of phosphines to stabilise the low oxidation states of metal atoms makes them useful for homogeneous catalysis.<sup>1</sup> Additionally, phosphines promote the solubility of metal complexes in a wide range of organic solvents.<sup>1</sup> Changes in the properties of phosphorous ligands and their transition metal complexes are observed by changing the substituents on the ligands.<sup>7</sup>

Alicyclic carbon compounds have a three-dimensional structure that can increase the steric volume of alicyclic phosphine ligands by extending the three-dimensional spatial structure of the molecule. Alicyclic carbon compounds are also very stable, which may enable alicyclic phosphine ligands to further stabilise the catalyst.<sup>8-11</sup>

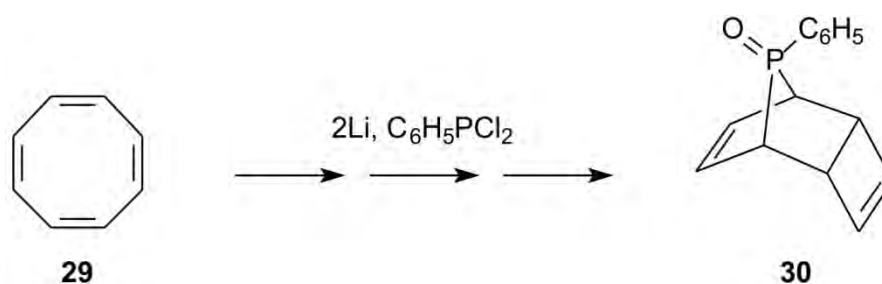
The commercially available Grubbs first generation precatalyst ( $\text{Ru}(\text{=CHPh})\text{Cl}_2(\text{PCy}_3)_2$ ), Grubbs 1) (**A1**, **Figure 1.1**) contains the strong electron donating group  $\text{PCy}_3$ .<sup>12</sup> The Ru-alkylidene fragment is not as nucleophilic as the alkylidene of the Schrock-type complexes.<sup>12</sup> The five-coordinate, 16-electron metal centre is very stable towards water, acid and various functional groups. The Grubbs 1 precatalyst (**A1**) is useful for ring-opening metathesis polymerisation (ROMP), and ring-closing metathesis (RCM).<sup>12</sup> The thermal stability, lifetime and activity of Grubbs 1 was improved by replacing one of the  $\text{PCy}_3$  groups with an N-heterocyclic carbene (NHC) ligand to form the second generation Grubbs precatalyst, **A2** (Grubbs 2).<sup>13,14</sup>

In a 2004 publication, Forman *et al.*<sup>15</sup> reported the new Phobcat precatalyst, **A3**, using the alicyclic phosphine 9-cyclohexyl-9-phospha-9H-bicyclononane as a new ligand for **A1**.<sup>16-18</sup> Precatalyst **A3** was tested on various metathesis reactions and it was found that the precatalyst showed better stability at higher temperatures, higher activity and better selectivity.<sup>15</sup> The success of the alicyclic phosphine in the **A3** precatalyst system serves as motivation to investigate other alicyclic phosphine compounds that might serve as ligands for **A1**.



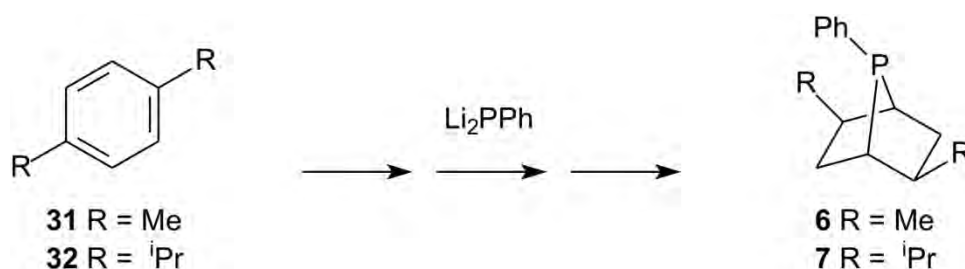
**Figure 1.1** The precatalysts investigated in this study. **A** indicates the first step in the metathesis reaction; **L** indicates ligands **4** to **8** and **10** to **28**. This **AL** numbering format will be used throughout the text to avoid having to renumber the structures and thus avoiding having multiple notations for the same structure in one text.

Compound **30** could be successfully synthesised from the work done by Katz *et al.*,<sup>19-21</sup> Quin *et al.*,<sup>22</sup> and Marx<sup>23</sup> (**Scheme 1.1**). Unfortunately, compound **30** only offers limited options for the manipulation of the steric bulk and electronic properties of the ligand. One way to overcome this limitation is compounds **6** and **7** (**Scheme 1.2**).



**Scheme 1.1** Ligand **30** offers limited options for the manipulation of the steric bulk and electronic properties of a Grubbs-type precatalyst.

In 1997, Zhu *et al.*<sup>24</sup> and Chen *et al.*<sup>25</sup> reported the multi-step synthesis of **6** and **7** from **31** and **32** through the addition of the dilithium salt of phenylphosphine,  $\text{Li}_2\text{PPh}$  (**Scheme 1.2**). Compounds **6** and **7** offer a potential easy and effective method to manipulate the steric bulk and electronic properties of the ligands. By manipulating the functional group R in the starting compound, various new phosphine ligands can be synthesised for **A1**. No evidence could be found in literature of these alicyclic phosphine compounds being used as ligands for **A1**.



**Scheme 1.2** Ligands **6** and **7** offer more options for the manipulation of the steric bulk and electronic properties of a Grubbs-type precatalyst than ligand **30**.

Organometallic chemists have been trying for more than 50 years to quantify the properties of transition-metal complexes in terms of the stereoelectronic properties of the ancillary ligands.<sup>26-29</sup> Such quantification would in principle be useful as a probe into the mechanism and to predict and control the reactivity, stereochemistry, and regiochemistry of stoichiometric and catalytic reactions involving phosphines, phosphine complexes, and other related ligands.<sup>30</sup> In order to investigate the electronic properties of ligands, a probe needs to be found that responds effectively and sensitively to changes in the electronic properties of the ligands.<sup>30</sup>

Over the last decade, molecular modelling has been successfully used in the study of chemical reactions catalysed by transition metals.<sup>31-33</sup> Molecular modelling provides a powerful tool to study the catalytic reaction mechanism of alkene metathesis, where ruthenium carbenes are used, before arduous synthesis of these ligands is attempted. Complete studies of the Grubbs-type precatalyst systems are very limited.<sup>32,33</sup>

## 1.2 Aim of the study

In literature, only limited attention has been paid to acyclic phosphine compounds that can be used as ligands for the Grubbs-type catalyst system.

The first aim of this study is to attempt to identify a phosphine-ligated Grubbs-type precatalyst for alkene metathesis with molecular modelling; to study the complete catalytic cycle of the precatalyst systems **AL**, **Figure 1.1**; and to determine whether phosphine compounds **4** to **8** and **10** to **28** will be suitable new ligands for the Grubbs-type precatalyst systems.

The second aim of this study is to attempt to identify the steric properties of the ligands and catalytic cycle steps with the Solid-G program as well as by means of the measurement of the various bond angles and lengths.

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